INFLUENCE OF ADDITIVES ON THE ELECTRODEPOSITION OF COPPER

C. Rajeswari, J. Bakkialakshmi, S. Mohan*, N.G. Renganathan
Central ElectroChemical Research Institute, Karaikkudi, India 630 006.

INTRODUCTION

Electrodeposition of Copper is of great significance in ULSI fabrication. Additives play a great role in the brightness, orientation and smoothness of the deposit. Deposition and dissolution processes of Copper are significantly affected by the diffusion of cupric ions from the bulk to the electrode surface [1]. An attempt has been made in this paper to understand the underlying kinetics of electrodeposition of Copper by estimating the diffusion co-efficient of cupric ions in the presence and absence of additives.

EXPERIMENTAL

Copper is electrodeposited using the standard bath employing the additives Polyethylene glycol [PEG] and Thiourea of analytical reagent grade at room temperature. Solutions were prepared in double distilled water. Platinum was used as the working and counter electrodes. SCE was used as the reference. Cyclic voltammograms were obtained for each concentration of each of the two additives under various scan rates.

RESULTS AND DISCUSSION

The diffusion coefficient was got from a plot of Peak current Vs. Scan rate using the relation $i_p = [(2.69 \times 10^5)\ n^{3/2} A D^{1/2} C_O^*]\ \nu^{1/2}$. Then a plot of diffusion coefficient of cupric ions in the presence and absence of each additive was made against the concentration of each additive. They are Fig.1 and Fig.2. for PEG and Thiourea respectively.

PEG acts as a levelling agent in the eletrodeposition of copper [3]. When PEG is added the deposition potential of copper is shifted to more negative potentials. This is due to the inhibitory effect of PEG on copper deposition. The cathodic current density also decreases with increase in concentration of PEG, due to the deceleration of rate of copper deposition. Thiourea acts as a brightener in copper electrodeposition [2,4]. When thiourea is added to the copper sulphate bath, a pattern similar to that of PEG is observed. Thiourea inhibits crystal growth of copper and favours nucleation process [5].

From the Fig.1 and Fig.2, it is clear that D (the diffusion co-efficient) of cupric ions decreases upto a certain concentration of the additives in the bulk (upto 4 g/l in the case of PEG and 2g/l in the case of thiourea), and then increases. In both the cases, it is evident that upto the inflection point the inhibitory effect of additives exist and with any further increase in the additive concentration, the mechanism changes and the rate of deposition of copper is enhanced. Hence in any plating bath, the concentration of additives must not exceed this limiting value. The results will be discussed in detail in the paper.

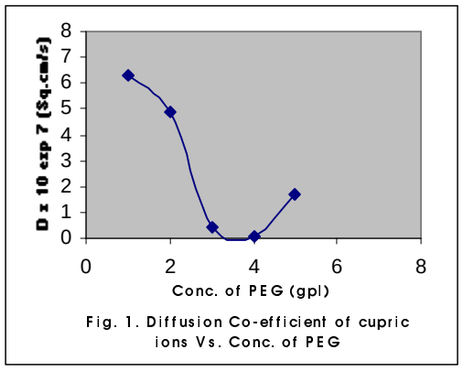

Fig. 1. Diffusion Co-efficient of cupric ions Vs. Conc. of PEG

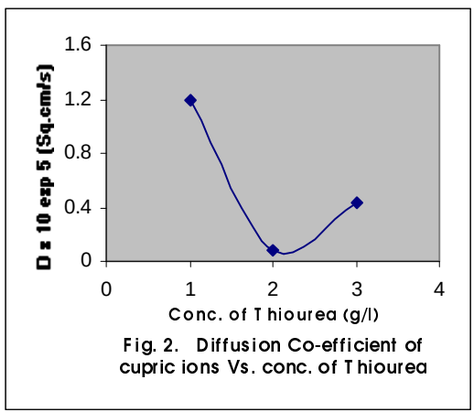

Fig. 2. Diffusion Co-efficient of cupric ions Vs. conc. of Thiourea

REFERENCES

1. Michael S. Moats, et al, Hydrometallurgy **56** (2000), 255-268
2. Liana Mures, et al, Hydrometallurgy **54** (2000), 161-169
3. D. Stoychev, Trans. IMF **76(2)** (1998), 73
4. Baconke, John H. Hoekstra, et al, J. Electrochem. Soc. **106(5)** ,382
5. E.E. Farndon et al, J. Applied Electrochem. **25** (1995), 574-583

* Author for Correspondence